ACTIVATIONLESS ELECTRON TRANSFER PROCESSES IN BIOLOGICAL SYSTEMS

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1. Introduction

Electron transfer (ET) processes between ions in solutions [1], as well as in biological systems [2,3], can adequately be described within a unified theoretical framework in terms of non-adiabatic multiphonon non-radiative processes [2–4]. A central prediction of the theory [2–4] is that at sufficiently low temperatures the ET rate is constant and independent of temperature manifesting the effects of nuclear tunnelling, while at high temperatures the rate exhibits the conventional Arrehnius-type activated temperature dependence. This pattern has been observed for the DeVault-Chance ET process between cytochrome and the reaction centre in chromatium [5]. Experimental studies of the primary charge separation steps in bacterial photosynthesis [6,7] have established that several of the elementary ET processes are temperature independent over a wide temperature range [8]. The ET process between bacteriopheophtin (BPh) and ubiquionone-10 (Q) [6–8]:

$$(BChl)_2^+BPh^-Q \rightarrow (BChl)_2^+BPhQ^- \qquad (A)$$

where $(BChl)_2$ represents the chlorophyll dimer, is characterized by a rate [6,7] $W = 7 \times 10^9\ s^{-1}$, which is temperature independent [8] over the range 4–300 K. The back reaction [9]:

$$(BChl)_2^+BPhQ^- \rightarrow (BChl)_2BPhQ \qquad (B)$$

is slow, the rate being $W \simeq 10^2\ s^{-1}$, which is again temperature independent in the range 4–300 K. Another interesting class of ET process in the category is ET from a cytochrome donor, C, to the reaction centre, P^+, in the photosynthetic bacterium *Rhodospirillum rubrum* [10,11]:

$$C + P^+ \rightarrow C^+ + P \qquad (C)$$

Here, the low temperature rate is $W = 40\ s^{-1}$, being temperature independent in the range 4–50 K, while in the region 50–300 K the rate W slightly decreases with increasing temperature [10,11]. The temperature independent rates for reactions (A)–(C) cannot be reconciled with low temperature nuclear tunnelling, which will be followed by an activated rate at higher temperatures. For such conventional non-adiabatic ET processes nuclear tunnelling is exhibited in the temperature range where the thermal energy, k_BT, with k_B being the Boltzman factor and T the absolute temperature, is considerably smaller than the characteristic vibrational frequency $\hbar\omega$. The transition temperature T_a marking the onset of activated ET is [12] $k_BT_a = \hbar\omega/4$, so that for reactions (A)–(C) one gets $\hbar\omega > 1000\ cm^{-1}$, which is definitely too high for a vibrational mode suffering a large configurational distortion during the ET process [2,3]. A way out of this dilemma is to attribute reactions (A)–(C) to activationless ET processes (AETP), where the nuclear potential surfaces for the initial and for the final states cross at the minimum of the initial state. The assignment of reaction (B) to AETP was given in [13], while the attribution of reaction (A) to such AETP is in accord with the suggestions in [8,12]. In this note we utilize the theory of non-adiabatic multiphonon ET processes [3,4] to explore the characteristics of such AETPS demonstrating that:

(1) They correspond to exoergic processes.
(2) The configurational nuclear changes involved are optimal to ensure the fastest reaction rate, whose magnitude is restricted only by the electronic coupling.
(3) The rate constant is temperature independent over a broad temperature range.
(4) The low temperature rate is determined essentially by the electronic coupling and not by nuclear

contributions.

(5) At higher temperatures these processes exhibit an apparent negative activation energy.

Consider ET from a thermally-equilibrated initial nuclear potential surface U_{DA} corresponding to the donor (D)–acceptor (A) pair DA to the final nuclear potential surface $U_{D^+A^-}$ which corresponds to the oxidized donor (D^+)-reduced acceptor (A^-) pair D^+A^-. A simple description of these two potential surfaces can be given in terms of the two configurational diagrams portrayed in fig.1:

$$U_{DA}(q) = (\hbar\omega/2)\, q^2 \qquad (1)$$

$$U_{D^+A^-}(q) = (\hbar\omega/2)\,(q - \Delta)^2 + \Delta E \qquad (2)$$

Here q is the nuclear coordinate in dimensionless units, being normalized to the zero-point RMS displacement. Δ is the horizontal displacement of the minima of the potential surface expressed again in dimensionless units. ΔE is the electronic energy gap, representing the vertical displacement of the minima of the potential surfaces. It will be convenient to define the reduced energy gap:

$$p = |\Delta E|/\hbar\omega \qquad (3)$$

The electron-vibration coupling strength is:

$$S = \Delta^2/2 \qquad (4)$$

while the medium rearrangement energy is:

$$E_S = S\hbar\omega \qquad (4a)$$

This simple single mode approximation incorporates all the necessary physical features of the problem. This model can be extended to include the dispersion of optical medium modes and the role of simultaneous coupling with medium modes and intramolecular vibrations. We shall now focus attention on exoergic ET processes, where $\Delta E < 0$ (and $p > 1$), and consider three limiting cases:

(a) Weak coupling limit $S \leqslant 1$, so that $p > S$. This physical situation corresponds to slight displacement of the two potential surfaces and where tunnelling occurs from a broad range of vibronic levels.

(b) Strong coupling situation $S > 1$. Now the potential surfaces intersect not far from the minimum of the initial surface.

(c) Very strong coupling situation, $S \gg 1$ and $S \gg p$. When the coupling S further increases the minimum of the initial state it is located outside the crossing point of the potential surfaces.

The transition from the strong coupling situation (b) to the very strong coupling limit (c) is characterized by the condition $E_S = -\Delta E$, i.e., $p = S$, which for exoergic processes is characterized by the crossing of the potential surfaces at the minimum of the initial state. This physical situation corresponds to an activationless ET process.

The theory of non-adiabatic multiphonon ET processes results in an ET rate, W, which is expressed in terms of an electronic coupling term:

$$A = 2\pi|V|^2/\hbar^2\omega \qquad (5)$$

with V being the two-centre electron transfer integral, and a Franck-Condon vibrational overlap factor. The temperature-independent rate at low temperatures is [4]:

$$W = A \exp(-S) S^p/p! \qquad (k_B T \ll \hbar\omega) \qquad (6)$$

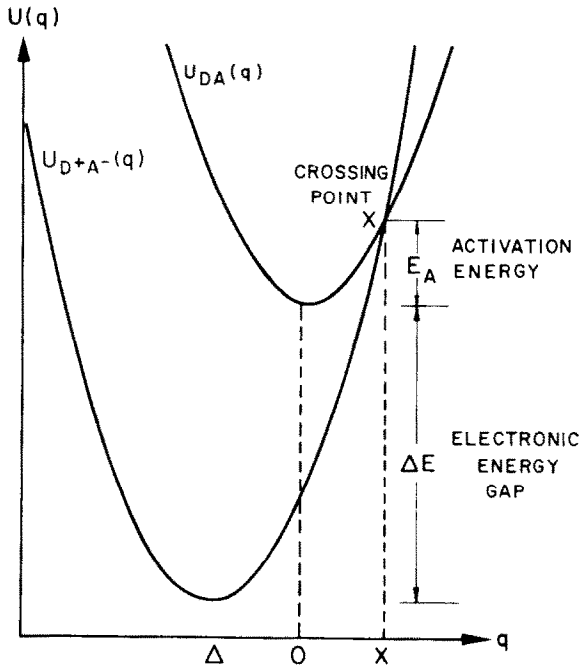

Fig.1. Nuclear potential surfaces for an electron transfer process. The initial nuclear potential surface $U_{DA}(q)$ represents the donor–acceptor pair DA, while the final potential surface $U_{D^+A^-}(q)$ corresponds to the D^+A^- pair. q is the nuclear coordinate in dimensionless units (see text). The minimum of the initial potential surface is located at $q = 0$, while the minimum of the final potential surface is located at $q = \Delta$. The electronic energy gap ΔE and the activation energy E_A are marked.

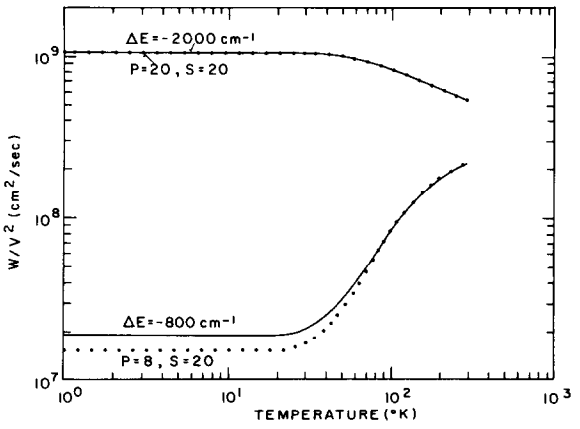

Fig.2. Model calculations for the temperature dependence of ET rate for activated and for activationless processes. Solid line represents the result of model calculations for a square distribution of medium optical phonon modes $\eta(\omega) = E_S/(\hbar\omega_0\Delta\omega)$ with $E_S = 2000\ cm^{-1}$, $\hbar\omega_0 = 100\ cm^{-1}$, $\Delta\omega/\omega_0 = 0.4$. Dotted lines were calculated for the single mode approximation (eq. (4) of [3]) with the mean frequency $\hbar\omega = 100\ cm^{-1}$ and $E_S = 2000\ cm^{-1}$.

which for exothermic processes characterized by a sufficiently large value of p can be recast in the form:

$$W = A(2\pi p)^{-1/2} \exp(-S - \gamma p); \quad \gamma = \ln(p/S) - 1 \tag{7}$$

While the activated rate at high temperatures is given by [3,4]:

$$W = A(\hbar\omega/4\pi S k_B T)^{1/2} \exp(-E_A/k_B T); \quad (k_B T >> \hbar\omega) \tag{8}$$

where the activation energy being:

$$E_A = (p - S)^2 \hbar\omega/4S \tag{9}$$

For activationless processes $p = S$, so that it is immediately apparent from eq. (7) and eq. (9) that $E_A = 0$ and $\gamma = -1$. The low temperature rate is:

$$W = A/(2\pi p)^{1/2} \tag{10}$$

while the high temperature rate takes the form:

$$W = A(\hbar\omega/4\pi S k_B T)^{1/2} \tag{11}$$

From eq. (10) and eq. (11) it is apparent that:

(i) The low temperature rate for AETP, eq. (10), reflects an ET process which occurs from the lowest vibrational level of the initial state and which is independent of temperature.

(ii) The high temperature rate for AETP, which exhibits the temperature dependence $W\alpha T^{-1/2}$, decreases with increasing temperature. Thus the ET rate is characterized by a negative apparent activation energy. The retardation of the ET rate with increasing temperature can be readily rationalized by noting that the fast microscopic ET process occurs from the vibrationless level of the initial state at the crossing, while the microscopic rates from higher vibrational levels are slower.

(iii) The temperature T_0, which characterizes the crossing from the temperature-independent region to the range characterized by the negative apparent activation energy for activationless processes, is $k_B T_0 \sim \hbar\omega/2$, while the ratio of the low temperature rate (10) and the high temperature rate (11) is $(2k_B T/\hbar\omega)^{1/2}$.

To provide a visual demonstration of the general features of AETPs, we have performed model calculations for a system whose electron phonon coupling is characterized by the square distribution $\eta(\omega) = E_S/(\hbar\omega_0\Delta\omega)$, where $\hbar\omega_0$ is the mean value and $\hbar\Delta\omega$ the distribution width. These results for the activationless case, where $\Delta E = -E_S$, as well as for an activated situation, are presented in fig.2. These calculations were performed using the saddle point approximation [4,14] for the ET rate. In fig.2 we have also presented the rates calculated from the single-mode approximation (eq. (4) of [3]). The agreement between the rates, which incorporate the phonon dispersion and those obtained within the single-mode approximation, inspires confidence in our general analysis which rests on a single-mode model.

The last point we have to consider pertains to the absolute values of the ET rates of eq. (1)–(3), which can vary by 10 orders of magnitude for ET processes in various systems. The low T rate for the AETP is:

$$W = 4.7 \times 10^{11} (|V|/cm^{-1})^2/(\hbar\omega/cm^{-1}) p^{1/2}\ s^{-1} \tag{12}$$

The $1e^-$ 2-centre electron transfer integral V depends strongly on the separation R and on the relative orientation of the electron donor and acceptor. As V is essentially determined by the overlap of the tails of the electronic wavefunctions, we expect that it can be crudely represented in the form [2,3]:

$$V = V_0 \exp(-\alpha R) \quad (13)$$

Utilizing the numerical results [14] for a many-electron calculation of V for nearest-neighbour interaction between two aromatic molecules, such as naphthalene and anthracene, we get $V_0 \simeq 1 \times 10^5$ cm^{-1} and $\alpha = 1.0$ Å^{-1}. Thus, the activationless low temperature rate, eq. (12), provides a direct determination of the electronic coupling and a very rough estimate of the distance scale for the ET process [2,3]. For reaction (A), which is expected to be dominated by a nuclear contribution from intramolecular high frequency vibrational modes, we take $\hbar\omega = 500$ cm^{-1} originating from the metal ligand stretching mode [2,3,5] and choose a reasonable value of $\Delta E = 2000$–4000 cm^{-1}, i.e., $p = 4$–8, for the energy gap. We then get $V \simeq 4$ cm^{-1} which corresponds, according to eq. (13), to a close donor–acceptor spacing of $R \simeq 10$ Å. The same frequency and energy gap in the case of reaction (B) determine $V \simeq 5 \times 10^{-4}$ cm^{-1}, which is in accord with the estimate in [13] of $V \simeq 8 \times 10^{-4}$ cm^{-1} and which, according to eq. (13), corresponds to a large donor–acceptor spacing of $R \simeq 19$ Å. The temperature independence of the AETPs (A) and (B) implies that $k_B T_0 \geqslant 200$ cm^{-1} for the crossing temperature, whereupon $\hbar\omega \geqslant 400$ cm^{-1}, which is in accord with our estimate of the vibrational frequency $\hbar\omega = 500$ cm^{-1} for the mode which undergoes an appreciable configurational change during ET. The weak temperature dependence of the rate of reaction (C), which decreases by a factor of ~2 in the range $T = 50$–300 K is consistent with the predictions of an apparent negative activation energy for AETP. For reaction (C) the crossing temperature is rather low implying that low frequency vibrational modes with $\hbar\omega_P \sim 100$ cm^{-1} may also be involved in that AETP process. Such a continuous spectrum of polar medium modes of ~100 cm^{-1} also has a pronounced effect in the DeVault-Chance ET process between cytochrome and the reaction centre in chromatium [15].

From the foregoing discussion it is apparent that for AETP the intramolecular organization, involving the nuclear distortions of the donor and of the acceptor centres, is optimal to ensure the most efficient ET rate. The absolute magnitude of the rate is determined by intermolecular organization, pertaining to the spatial arrangement and spacing of the donor and acceptor centres.

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